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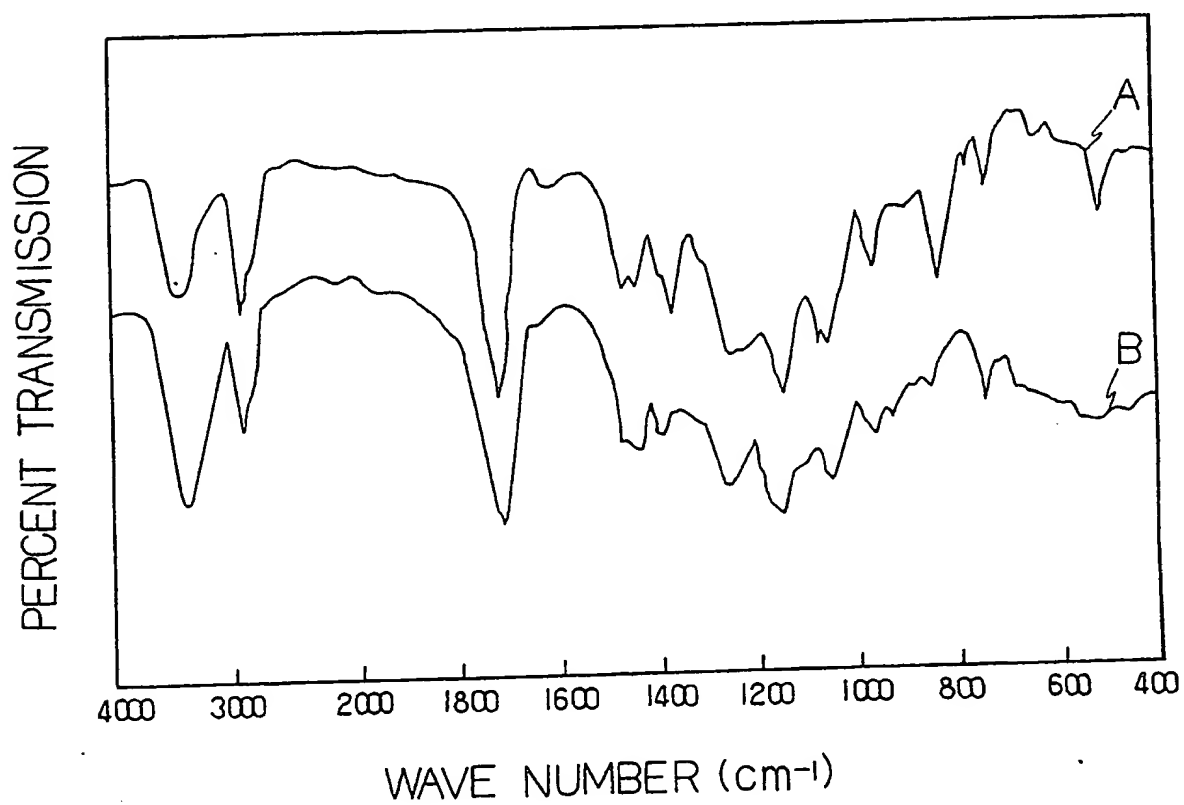
(54) Contact lens prepared by
copolymerising ketalised glycitol
monomer

(57) A water-absorptive contact lens
is prepared by polymerizing a
monomer mixture containing a
monomer having a ketalized glycitol
and a hydrophilic monomer and/or a

hydrophobic monomer, and after
forming the resulting copolymer into a
contact lens, treating the contact lens
with an acid to convert the ketal
groups into hydroxyl groups and
replacing the acid in the lens with
water or saline. The contact lens has
excellent oxygen permeability and
affinity for the eye and can be worn
continuously for a long period of time.

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SPECIFICATION

Contact lens and process for preparing the same

The present invention relates to a novel water-absorptive contact lens and a process for the preparation thereof.

5 Various water-absorptive contact lenses have hitherto been known, and among them, a contact lens having a water content of 30 to 40% by weight made of a polymer comprising predominantly 2-hydroxyethyl methacrylate is the most popular. However, this water-absorptive contact lens made of the 2-hydroxyethyl methacrylate polymer has no sufficient permeability to oxygen of an amount required physiologically in the cornea of the eye. Therefore, it is impossible to wear the lenses over about 16 10 hours a day, and the wearing over this limit is dangerous because of causing disturbance of the corneal tissue.

For such a reason, attempts have been made to develop contact lenses having a higher water content with the object of increasing the water content, thereby supplying a physiologically sufficient amount of oxygen for the cornea from the atmosphere to the cornea through a large amount of water 15 contained in the contact lens material. The most general material for such high water content contact lenses is copolymers of a major amount of N-vinyl pyrrolidone and a minor amount of a methacrylate compound, e.g. 2-hydroxyethyl methacrylate and alkyl methacrylates such as methyl methacrylate. These copolymers have an ability to absorb water usually in an amount of about 50 to about 80% by weight. Many of these high water content contact lenses are able to supply a sufficient amount of 20 oxygen from the atmosphere to the cornea through water impregnated in the lens materials. However, they have the defects that due to high water content, the strength of the lens materials is low and the lens contour is unstable, and therefore they are not sufficiently popularized. Also, wear of high water content contact lenses made of such a vinyl pyrrolidone polymer tends to cause keratitis diffusa superficialis frequently, and this fact is also one of major causes of hindering the popularization of the 25 high water content contact lenses. Like this, the oxygen permeability of a contact lens material is a necessary condition in providing a water-absorptive contact lens which can be continuously worn for a long period of time, but not a sufficient condition.

It is known that in addition to the oxygen permeability of a lens material, the affinity of the lens material for the eye tissue, especially the corneal tissue, is a large factor for providing a water- 30 absorptive contact lens which can be worn continuously on the eye for a long period of time. However, there is no standardized method of confirming the affinity of a lens material for the eye tissue, and this makes it more difficult to develop a better contact lens of water-absorptive type.

It is attempted to copolymerize a dihydroxyalkyl acrylate or methacrylate, especially glycerol methacrylate (2,3-dihydroxypropyl methacrylate), with various copolymerizable monomers to provide a 35 water-absorptive contact lens material. U.S. Patent No. 3,957,362 discloses a copolymer of glycerol methacrylate and an alkyl methacrylate such as methyl methacrylate, and U.S. Patent No. 4,056,496 discloses a copolymer of glycerol methacrylate, an alkyl methacrylate and a slight amount of a water-insoluble epoxidized alkyl methacrylate. Also, U.S. Patent No. 4,267,295 discloses a copolymer of glycerol methacrylate, an alkyl methacrylate and a hydrophilic monomer such as 2-hydroxyethyl 40 acrylate. However, the water content of these conventional copolymers is equal to or only slightly higher than the water content, i.e. 30 to 40% by weight, of a polymer comprising predominantly 2-hydroxyethyl methacrylate. Such a degree of water content is insufficient for supplying oxygen necessary for the metabolism of the cornea from the atmosphere through water included in the lens material. In these prior art, glycerol methacrylate used as a main component is prepared by hydrolysis of glycidyl 45 methacrylate or hydrolysis of isopropylideneglycerol methacrylate. In case of the former process, a trace amount of glycidyl methacrylate inevitably remains in the produced glycerol methacrylate, and it functions as a cross-linking agent upon the polymerization of glycerol methacrylate. In addition, ether bonds are easy to be formed between the hydroxyl groups in the side chains of glycerol methacrylate. Consequently, the cross-linking density of the obtained copolymer becomes high and increase of the 50 water content is inhibited. Also, in case of using glycerol methacrylate prepared by the latter process, increase of the water content is inhibited in the same manner by the formation of ether bonds. Therefore, it is difficult to obtain a contact lens having an oxygen permeability sufficient for continuously wearing for a long period of time from the glycerol methacrylate copolymers according to these prior art processes.

55 It is an object of the present invention to provide a water-absorptive contact lens which has a sufficient water content for supplying oxygen to the cornea of the eye and moreover has an excellent affinity for the eye tissue.

A further object of the invention is to provide a water-absorptive contact lens which can be worn continuously for a long period of time.

60 Another object of the invention is to provide a process for preparing a water-absorptive contact lens.

These and other objects of the present invention will become apparent from the description hereinafter.

It has now been found that the above-mentioned objects can be attained by copolymerizing a

monomer having a ketalized glycitol with other copolymerizable monomers such as hydrophilic monomers and hydrophobic monomers to produce a copolymer having ketalized glycitol groups as side chains and treating the copolymer with an acid to convert the ketal groups into hydroxyl groups.

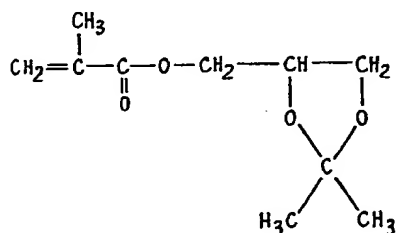
In accordance with the present invention, there is provided a water-absorptive contact lens prepared by a process which comprises the steps of carrying out a polymerization of a monomer mixture containing a monomer having a ketalized glycitol and at least one member selected from the group consisting of a hydrophilic monomer and a hydrophobic monomer, forming the resulting copolymer into a contact lens, treating the contact lens with an acid and replacing the acid impregnated in the resulting water-absorptive contact lens with water or a physiological saline water.

The accompanying drawing is infrared absorption spectra of a copolymer before and after an acid treatment which is used as a contact lens material in the present invention.

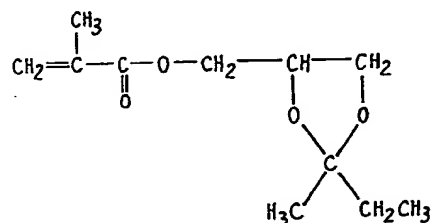
In the present invention, a water-absorptive contact lens made of a polymer containing as an essential component the monomer units having glycitol as side chains is prepared by a process in which hydroxyl groups of a monomer having a glycitol are protected previously by ketalization, the monomer having a ketalized glycitol is copolymerized with other copolymerizable monomers, the obtained copolymer is formed into a contact lens having a desired shape, the contact lens is treated with an acid to cause the deketalization, thereby converting the ketal groups in the copolymer into hydroxyl groups. Therefore, increase of the cross-linking density due to the formation of ether bonds, etc. in the copolymerization, as seen in the before-mentioned prior art, can be prevented and consequently copolymers having a high water contact and characteristics desirable as a contact lens material can be easily obtained.

The monomer having a ketalized glycitol (hereinafter referred to as "ketalized glycitol monomer") used in the present invention includes, for instance, ester compounds of a ketalized glycitol with an ethylenically unsaturated carboxylic acid such as acrylic acid or methacrylic acid, and ether compounds of a ketalized glycitol with an ethylenically unsaturated alcohol such as allyl alcohol.

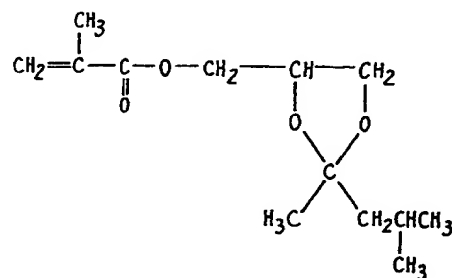
Typical examples of the ketalized glycitol acrylate and methacrylate are 2,3-O-isopropylideneglycerol methacrylate (hereinafter referred to as "IPGMA") of the formula:



2,3-O-isopropylideneglycerol acrylate, 2-methyl-2-ethyl-4-methacryloyloxymethyl-1,3-dioxolan (hereinafter referred to as "MEMA") of the formula:

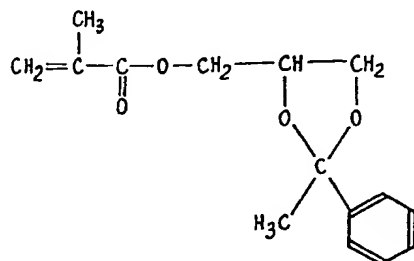


2-methyl-2-ethyl-4-acryloyloxymethyl-1,3-dioxolan, 2-methyl-2-isobutyl-4-methacryloyloxymethyl-1,3-dioxolan (hereinafter referred to as "MBMA") of the formula:

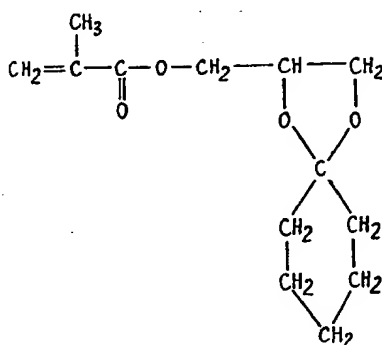


2-methyl-2-isobutyl-4-acryloyloxymethyl-1,3-dioxolan, 2-methyl-2-phenyl-4-methacryloyloxymethyl-

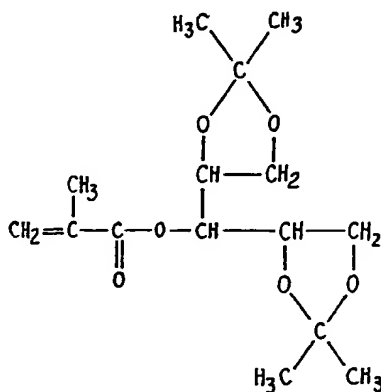
1,3-dioxolan (hereinafter referred to as "MPMA") of the formula:



2-methyl-2-phenyl-4-acryloyloxymethyl-1,3-dioxolan, 2-methacryloyloxymethyl-1,4-dioxaspiro[4,5]decane (hereinafter referred to as "2-MSDD") of the formula:



2-acryloyloxymethyl-1,4-dioxaspiro[4,5]decane, 1,2:4,5-di-(O-isopropylidene)xylitol-3-methacrylate (hereinafter referred to as "3-MDIX") of the formula:



and 1,2:4,5-di-(O-isopropylidene)xylitol-3-acrylate.

The ketalized glycol acrylates and methacrylates are prepared, for instance, by ketalizing a glycol having the general formula (I):

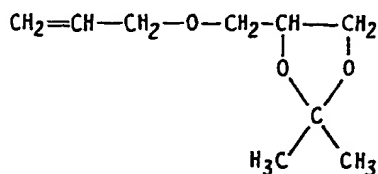


wherein n is an integer of 1 to 5, with a ketone compound such as acetone, methyl ethyl ketone, cyclohexanone, acetophenone or methyl isobutyl ketone, and then reacting the ketalized glycol with an acryloyl or methacryloyl halide to introduce the polymerizable group into the residual hydroxyl group.

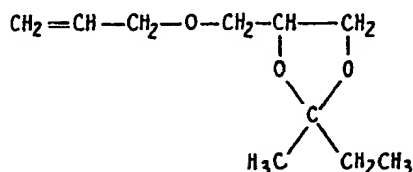
The glycol of the above general formula (I) wherein n is 1 or 3 is preferred, since the reaction is easy to proceed. Some ketalized glycol acrylates and methacrylates such as IPGMA, MEMA and 2-MSDD can also be prepared directly by reacting glycidyl acrylate or glycidyl methacrylate with the above-mentioned ketone compound such as acetone or methyl ethyl ketone in the presence of an acid such as Brønsted acid or Lewis acid.

Typical examples of the ketalized glycol ether are allyl isopropylideneglycerol ether (hereinafter

referred to as "ALIPG") of the formula:

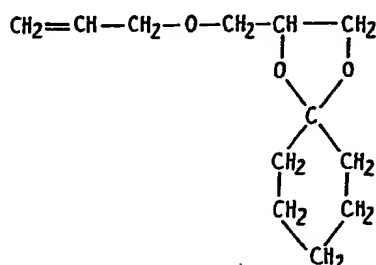


4-allyloxymethyl-2-methyl-2-ethyl-1,3-dioxolan (hereinafter referred to as "ALME") of the formula:



5 2-allyloxymethyl-1,4-dioxo-spiro[4,5]decane (hereinafter referred to as "ALCH") of the formula:

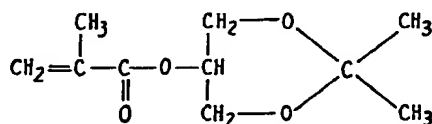
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10 The ketalized glycolol allyl ethers are prepared, for instance, by ketalizing the glycolol of the general formula (I) such as glycerin with various ketone compounds, and then reacting the ketalized glycolol with an allyl halide such as allyl chloride. The ketalized glycerol allyl ethers can also be prepared directly by reacting allyl glycidyl ether with various ketone compounds in the presence of an acid catalyst.

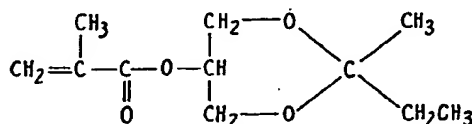
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Another example of the ketalized glycolol monomer used in the present invention are m-dioxane derivatives of acrylic or methacrylic acid such as 2,2-dimethyl-5-methacryloyloxy-1,3-dioxane (hereinafter referred to "DMDO") of the formula:

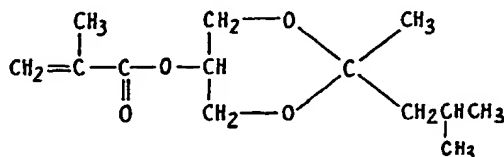


15 2,2-dimethyl-5-acryloyloxy-1,3-dioxane, 2-methyl-2-ethyl-5-methacryloyloxy-1,3-dioxane (hereinafter referred to as "MEDO") of the formula:

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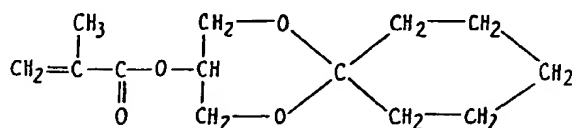
2-methyl-2-ethyl-5-acryloyloxy-1,3-dioxane, 2-methyl-2-isobutyl-5-methacryloyloxy-1,3-dioxane (hereinafter referred to as "MBDO") of the formula:



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2-methyl-2-isobutyl-5-acryloyloxy-1,3-dioxane, 3-methacryloyloxy-1,3-dioxo-spiro[5,5]undecane (hereinafter referred to as "MSDO") of the formula:



and 3-acryloyloxy-1,3-dioxaspiro[5.5]undecane. These compounds are all novel compounds, and can be obtained as by-products in the preparation of the ketalized glycerol acrylate or methacrylate from glycidyl acrylate or methacrylate.

The ketalized glycidyl monomers may be employed alone or in admixture thereof. In case of preparing a copolymer by employing the ketalized glycidyl ethers such as ALIPG, ALME and ALCH, the copolymer deketalized by the acid treatment thereof is relatively low in water absorbing ability. Therefore, preferably, the ketalized glycidyl ethers are employed in combination with other ketalized glycidyl monomers. Also, since the m-dioxane derivative type methacrylates or acrylates such as DMDO, MEDO, MBDO and MSDO are those obtained as by-products upon the direct preparation of the ketalized glycerol methacrylates or acrylates such as IPGMA, MEMA, MBMA and 2-MSDD from glycidyl methacrylate or acrylate, and since the isolation and purification are industrially disadvantageous due to necessity of repeated distillation and decrease of the yield, it is practical to employ them in the form of a mixture with the corresponding ketalized glycerol methacrylate or acrylate obtained as main product in the direct preparation thereof.

A part of the ketalized glycidyl monomer may be replaced with a ketalized monosaccharide methacrylate or acrylate such as 1,2:5,6-di-O-isopropylidene-3-O-methacryloyl-D-glucopyranoside (another name: 1,2:5,6-di-O-isopropylidene-3-O-methacryloyl-D-glucose), 1,2:3,4-di-O-isopropylidene-6-O-methacryloyl-D-galactopyranoside (another name: 1,2:3,4-di-O-isopropylidene-6-O-methacryloyl-D-galactose), 1-O-methacryloyl-2,3:5,6-di-O-isopropylidene-D-mannofuranoside (another name: 1-O-methacryloyl-2,3:5,6-di-O-isopropylidene-D-mannose), and the like. The same effects can be obtained by the use of such a mixture of the ketalized glycidyl monomer and the ketalized monosaccharide monomer.

The ketalized glycidyl monomers are copolymerizable with various monomers. The material for the water-absorptive contact lens of the present invention is prepared by copolymerizing the ketalized glycidyl monomers with at least one member selected from a hydrophilic monomer and a hydrophobic monomer.

Preferable examples of the hydrophilic monomer used in the present invention are, for instance, 2-hydroxyethyl methacrylate, 2-hydroxyethyl acrylate, 2-hydroxypropyl methacrylate, 2-hydroxypropyl acrylate, polyethylene glycol monomethacrylate, polyethylene glycol monoacrylate, methacrylamide, acrylamide, dimethylmethacrylamide, dimethylacrylamide, methacrylic acid, acrylic acid, N-vinyl pyrrolidone, and the like. These hydrophilic monomers may be employed alone or in admixture thereof.

Upon the deketalization to convert the ketal groups into hydroxyl groups by immersing a contact lens formed from the obtained copolymer in an aqueous solution of an acid, the copolymerization of the ketalized glycidyl monomer with these hydrophilic monomers facilitates uniform and effective permeation of the acid solution into the lens material, thus causing the deketalization efficiently. Also, in case of hydrophilic monomers such that the ability to absorb water of the homopolymer thereof is relatively low, e.g. 2-hydroxyethyl methacrylate and 2-hydroxypropyl methacrylate, it is possible to control the water content of the obtained contact lens to some extent by copolymerizing the ketalized glycidyl monomer with such hydrophilic monomers.

Preferable examples of the hydrophobic monomer used in the present invention are, for instance, alkyl esters of acrylic or methacrylic acid in which an alkyl group has 1 to 15 carbon atoms, such as methyl methacrylate, methyl acrylate, ethyl methacrylate, ethyl acrylate, butyl methacrylate, butyl acrylate, amyl methacrylate, amyl acrylate, cyclohexyl methacrylate, cyclohexyl acrylate, octyl methacrylate, octyl acrylate, decyl methacrylate, decyl acrylate, undecyl methacrylate, undecyl acrylate, lauryl methacrylate and lauryl acrylate, vinyl methacrylate, vinyl acrylate, allyl methacrylate, allyl acrylate, alkyl esters of itaconic acid or crotonic acid such as propyl itaconate and propyl crotonate, vinyl esters of aliphatic carboxylic acids such as vinyl acetate and vinyl propionate, styrene, acrylonitrile, and the like. These hydrophobic monomers may be employed alone or in admixture thereof. The use of the hydrophobic monomer is effective particularly for increasing the strength of the obtained water-absorptive contact lens and thus improving the durability of the lens, as well as controlling the water content of the lens. For these purposes, the methacrylic acid esters such as the alkyl ester, vinyl ester and allyl ester are particularly effective.

The amount of the ketalized glycidyl monomer is selected from 5 to 97 parts by weight, preferably 20 to 85 parts by weight, more preferably 40 to 80 parts by weight, per 100 parts by weight of the total amount of the ketalized glycidyl monomer and the hydrophilic monomer and/or the hydrophobic monomer. The ketalized glycidyl monomer is copolymerized with at least one of a hydrophilic monomer and a hydrophobic monomer. In case of employing the hydrophilic monomer, the amount thereof is selected from 3 to 95 parts by weight, preferably 15 to 80 parts by weight, more preferably 20 to 60 parts by weight, per 100 parts by weight of the total amount of the ketalized glycidyl monomer and the

hydrophilic monomer and/or the hydrophobic monomer. In case of employing the hydrophobic monomer, the amount thereof is selected from 1 to 40 parts by weight, preferably 1 to 20 parts by weight, more preferably 1 to 12 parts by weight, per 100 parts by weight of the total amount of the ketalized glycol monomer and the hydrophobic monomer and/or the hydrophilic monomer. When the amount of the ketalized glycol monomer is more than 97 parts by weight, the strength of the obtained contact lens is decreased, and when the amount is less than 5 parts by weight, the effects to be produced by its use become poor. Also, when the amount of the hydrophilic monomer is more than 95 parts by weight, the effects to be produced by the use of the ketalized glycol monomer become poor, and when the amount of the hydrophobic monomer is more than 40 parts by weight, the deketalization by acid treatment is hard to smoothly proceed.

Vinyl esters and allyl esters of methacrylic and acrylic acids among the above-mentioned hydrophobic monomers also act as a cross-linking agent, and accordingly they are preferably employed in an amount of not more than 2 parts by weight per 100 parts by weight of the total monomers used.

The above-mentioned ketalized glycol monomer and at least one of the hydrophilic and hydrophobic monomers are selected and admixed so that the mixture thereof contains the monomers in amounts within the above-mentioned respective ranges and the total amount of the monomers selected from the above three kinds of the monomers becomes 100 parts by weight.

A cross-linking agent having at least two polymerizable functional groups may be employed in the present invention for the purpose of improving the solvent resistance and shape stability of the obtained contact lens. Preferable examples of the cross-linking agent used in the present invention are, for instance, ethylene glycol dimethacrylate, ethylene glycol diacrylate, diethylene glycol dimethacrylate, diethylene glycol diacrylate, triethylene glycol dimethacrylate, triethylene glycol diacrylate, vinyl methacrylate, vinyl acrylate, allyl methacrylate, allyl acrylate, divinyl benzene, diallyl phthalate, trimethylolpropane trimethacrylate, and the like. These cross-linking agents may be employed alone or in admixture thereof. The amount of the cross-linking agent is selected from 0.01 to 2 parts by weight to 100 parts by weight of the mixture of the above-mentioned monomers.

The polymerization of the monomers is carried out by employing usual free radical polymerization initiators which are conventionally employed in the polymerization of unsaturated hydrocarbon compounds, e.g. benzoyl peroxide, azobisisobutyronitrile and azobisdimethylvaleronitrile. The polymerization initiators may be employed alone or in admixture thereof. They are employed usually in an amount of about 0.01 to about 1 part by weight to 100 parts by weight of the whole monomers used.

The polymerization may be carried out in the presence of, as a wetting agent, water or a substance which is soluble in water and is inert to the polymerization reaction, e.g. ethylene glycol, propylene glycol, butylene glycol, polyethylene glycol, polypropylene glycol and glycerin. The amount of the wetting agent is selected from about 2 to about 45% by weight based on the total amount of the whole monomers used and the wetting agent. The use of the wetting agent is not essential, but is very effective for the acid treatment of the copolymer for the deketalization, because the wetting agent is included in the obtained copolymer when the polymerization is carried out in the presence of the wetting agent by a bulk polymerization process. That is to say, even in the cases where the hydrophilic monomer is employed in a small proportion or is not employed, an acid solution can be effectively permeated into the lens material through the wetting agent impregnated in the lens material in a step of the acid treatment of the contact lens formed from the obtained copolymer, thus causing the deketalization efficiently. It is also possible to impart the toughness to the obtained copolymer so as to increase the processability in mechanical processing such as cutting by employing the wetting agent. The employed wetting agent can be easily replaced with water or a physiological saline water, for instance, by subjecting the acid-treated contact lens to neutralization treatment in an aqueous solution of an alkaline substance and immersing the lens in water or a physiological saline water, and if desired, further conducting the boiling treatment of the lens. The use of the wetting agent in an amount of more than 45% by weight is not desirable, because of being easy to cause trouble such as lowering of the optical property of the lens due to occurrence of white turbidity in the acid-treated lens material.

The polymerization and the formation into a contact lens shape can be conducted by usual techniques. For instance, the polymerization may be conducted in a mold corresponding to a shape of contact lens so as to directly provide a copolymer shaped in contact lens. The thus obtained contact lens may be further mechanically finished, as occasion demands. Also, the polymerization may be conducted in a suitable mold or container to form a contact lens material in the form of block, sheet or rod, and the lens material may be then mechanically processed in a usual manner such as cutting and polishing to give contact lenses of a desired shape. The copolymer obtained as a lens material has approximately the same molar composition as that of the polymerizable compounds used.

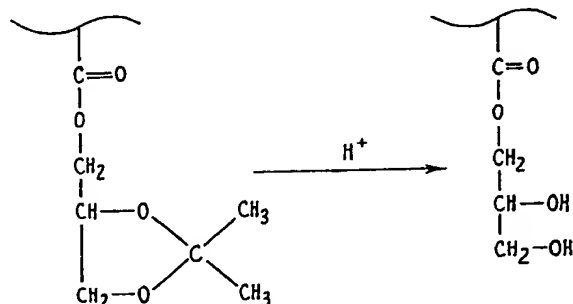
In general, the formation of a contact lens material having a high water-absorbing ability into a contact lens by mechanical processing has had to be made with paying great attention to the processing environment, particularly to the moisture control, because of high water-absorbing ability. According to the present invention, severe moisture control as required in the processing of a conventional water-absorptive contact lens is not necessary, since the hydroxyl groups of the glycol

monomer units in the copolymer are masked by ketalization and accordingly the water-absorbing ability

of the copolymer is decreased. Also, the coefficient of linear expansion of the swelled copolymer of the invention by subjecting the copolymer to the acid treatment, the neutralization treatment and then the hydration treatment is far smaller than that of a conventional water-absorptive contact lens material.

This fact is very desirable from the viewpoint of the accuracy in lens contour and shape in preparing a water-absorptive contact lens having a desired lens contour and shape which is used in water-swelled state, from a non-swelled lens material.

The copolymer in the form of a contact lens is treated with various organic and inorganic acids to convert the ketal groups in the copolymer into hydroxyl groups. For instance, as shown in the following reaction scheme, isopropylidene groups are eliminated by hydrolysis so as to make the copolymer hydrophilic.



Examples of the acid used in the above acid treatment are, for instance, hydrochloric acid, sulfuric acid, phosphoric acid, formic acid, acetic acid, trifluoroacetic acid, and the like. In case that the concentration of the acid used is high, there is the possibility of deterioration of the lens material and occurrence of crack. Therefore, it is desirable to conduct the acid treatment with raising gradually or stepwise the concentration of the aqueous treating liquor. Suitable acid concentration and immersion time vary depending on the material of the lens to be treated and the kind of the acid used, and cannot be absolutely defined. For instance, in case of hydrochloric acid, the treatment is usually made in a concentration of about 3 to about 20% by weight for about 3 to about 6 hours at room temperature. In case of formic acid or acetic acid, the treatment is usually made in a concentration of about 30 to about 90% by weight for about 2 hours to about 20 days at room temperature. In case of trifluoroacetic acid, the treatment is usually made in a concentration of about 80 to about 90% by weight for about 1 to about 2 hours at room temperature. In case that the material of the lens to be treated does not contain hydrophilic monomer units and moreover is not impregnated with a wetting agent, rapid causing of the deketalization reaction is liable to produce crack in contact lenses, and accordingly it is particularly desirable to conduct the acid treatment with increasing gradually or stepwise the concentration of acid in the treating liquor. In that case, the treatment may be carried out, for instance, by first immersing a contact lens in an aqueous acid solution of a low concentration, e.g. about 5% by weight, and then immersing it in an aqueous acid solution of a higher concentration.

The reaction caused by the above-mentioned acid treatment can be carried out with good reproducibility within a certain permitted limit without being strictly regulated by a standard treating method and a standard treating time, and accordingly the acid treatment as mentioned above is advantageously adoptable to an industrial practice.

The acid-treated contact lens may be further immersed in an aqueous solution of an alkaline substance such as sodium carbonate to neutralize the acid included in the lens. The acid-treated contact lens is usually immersed or boiled in water or a physiological saline water to remove the acid or wetting agent included in the lens.

The water-absorptive contact lens of the present invention can be continuously worn on the eye for a long period of time, since the lens has a high water content and accordingly has an excellent oxygen permeability, and moreover has an excellent affinity for the eye tissue in addition to softness and flexibility. Further, the contact lens of the invention has an excellent optical property, and also can be boiled in water for sterilization without impairing excellent characteristics of the lens.

The present invention is more specifically described and explained by means of the following Examples, in which all % are by weight unless otherwise noted. It is to be understood that the present invention is not limited to the Examples and various changes and modifications may be made in the invention without departing from the spirit and scope thereof.

The following Reference Example is also presented to illustrate one instance of the preparation of IPGMA which is a representative glycidol monomer used in the present invention.

REFERENCE EXAMPLE

(Synthesis of IPGMA from glycidyl methacrylate)

To a flask were added 15 g. (0.11 mole) of glycidyl methacrylate, 50 ml. (0.68 mole) of acetone and 100 p.p.m. of hydroquinone monomethyl ether, and 0.1 g. of silicotungstic acid tetracosahydrate

was further added to the flask with agitation. The reaction was carried out at room temperature for 28 hours. After the completion of the reaction, 10 g. of anhydrous sodium carbonate was added to the reaction mixture to neutralize the silicotungstic acid. After agitating for 1 hour, the reaction mixture was filtered with suction to remove a precipitate, and acetone was distilled away under reduced pressure from the filtrate. To the residue was added 200 ml. of n-hexane, and a polymeric material produced during the reaction was removed by filtration. To the filtrate were added 25 g. of anhydrous sodium sulfate and then 5 g. of active carbon, and the mixture was agitated and allowed to stand overnight. The mixture was filtered with suction, concentrated under reduced pressure and then purified by distillation under reduced pressure to give 12.5 g. (yield: 59.2%) of a colorless, transparent liquid having a boiling point of 60°C./0.2 mmHg. The product had a refractive index (n_D^{20}) of 1.442, and from this result and the infrared absorption spectrum, it was confirmed that the product was IPGMA.

Also, a part of the reaction mixture was taken out at the time of starting the reaction, and after 20 minutes and 20 hours from the starting, and at the end of the reaction (after 28 hours), and was examined by gas chromatography. It was found that glycidyl methacrylate was almost consumed after 20 minutes, and IPGMA and a by-product were produced in approximately equal amounts, that after 20 hours IPGMA increased while the by-product decreased, and that after 28 hours the by-product completely disappeared and only IPGMA was produced. That is to say, it was found that a by-product was temporarily produced in the course of the reaction, but finally only IPGMA was produced. Also, it was confirmed from the analytical results such as nuclear magnetic resonance spectrum that the by-product was DMDO.

Various ketalized glycol monomers such as MEMA, MBMA and 2-MSDD can be prepared in the same manner as in the Reference Example by employing various other ketones instead of acetone, e.g. methyl ethyl ketone, methyl isobutyl ketone and cyclohexanone. Simultaneously, the ketalized glycol monomers of dioxane derivative type such as MEDO, MBDO and MSDO can also be obtained as by-products in the course of the reaction, and if desired, the purity thereof can be raised by repeating the distillation.

EXAMPLE 1

There were mixed and dissolved 72.52 g. of IPGMA, 13.74 g. of n-vinyl pyrrolidone (hereinafter referred to as "N—VP"), 13.74 g. of methyl methacrylate (hereinafter referred to as "MMA") and 0.06 g. of azobisdimethylvaleronitrile (hereinafter referred to as "ADMVN") as a polymerization initiator. The mixture was placed in a test tube. The thermal polymerization was carried out stepwise at 40°C. for 24 hours in a constant temperature water bath, and then at 50°C. for 8 hours, at 60°C. for 6 hours, at 80°C. for 6 hours, at 100°C. for 3 hours and finally at 110°C. for 3 hours in a hot air circulating dryer to give a colorless, transparent polymer in the form of a rod. The rod was cut and polished in a usual manner to form into contact lenses.

The lenses were treated with an acid by immersing in 2N hydrochloric acid for 24 hours. After immersing in distilled water for 15 minutes, the lenses were then immersed in a 0.5% aqueous solution of sodium carbonate for 30 minutes to conduct the neutralization treatment. The lenses were further immersed in distilled water for 15 minutes, and boiled in a 0.9% physiological saline water for 1 hour. The thus obtained water-absorptive contact lenses were soft and flexible, and had a water content of 60.2%, an oxygen permeability of 2.46×10^{-10} ml.cm./cm.²sec.mmHg, a refractive index (n_D^{20}) of 1.391 and a visible ray percent transmission of more than 90%.

The water content was measured with respect to a lens impregnated with a 0.9% physiological saline water at 20°C. till saturation.

The oxygen permeability was measured at 35°C. in a 0.9% aqueous solution of sodium chloride by a platinum electrode method employing a film-oxygen gas permeameter of Seikaken type made by Rikaseiki Kogyo Kabushiki Kaisha.

The visible ray percent transmission was measured in a wavelength region of 780 to 380 nm. by Double-Beam Spectro Photometer Type UV—210 made by Shimadzu Corporation by employing a polymer film which was interposed between quartz plates.

The refractive index was measured by employing Abbé's refractometer made by Erma Optical Works Co., Ltd. and disk specimens.

COMPARATIVE EXAMPLE 1

Glycerol methacrylate was prepared according to the description of Example 1 of U.S. Patent No. 4,267,295 as follows:

To a flask were added 1 kg. of glycidyl methacrylate (commercially available under the commercial name "Acryester G" made by Mitsubishi Rayon Co., Ltd.), 1,500 ml. of distilled water and 2.5 ml. of concentrated sulfuric acid. The flask was placed on a water bath maintained at a temperature of 24° to 29°C., and the mixture was agitated for 6 days. The obtained reaction mixture was neutralized with a 10% aqueous solution of sodium hydroxide, and extracted with five 1 liter portions of an ether. The resulting water layer was saturated with sodium chloride, and the oil layer separated on the water layer was taken out and dissolved in methylene chloride. To the obtained solution was added anhydrous sodium sulfate, and it was allowed to stand in a cold and dark place for 16 hours. The solution was then

filtered to remove sodium sulfate, and methylene chloride was removed under reduced pressure by an evaporator on a cold water bath to give colorless, transparent liquid glycerol methacrylate.

Glycerol methacrylate, N—VP and MMA were admixed in amounts of 67.86 g., 16.07 g. and 16.07 g., respectively so that the molar ratio thereof agreed with the theoretical molar ratio of the glycerol methacrylate, N—VP and MMA components of the material constituting the water-absorptive contact lens finally obtained in Example 1. To the mixture was added 0.06 g. of ADMVN, and the polymerization was carried out under the same condition as in Example 1 to give a colorless, transparent polymeric material in the form of rod. The rod was cut and polished in a usual manner to form into contact lenses. The lenses were immersed in a 0.9% physiological saline water to hydrate and swell the lenses. The obtained contact lenses had a water content of 49.5%, an oxygen permeability of 1.47×10^{-10} ml.cm./cm.²sec.mmHg, a refractive index (n_D^{20}) of 1.412 and a visible ray percent transmission of more than 90%.

COMPARATIVE EXAMPLE 2

Glycerol methacrylate was prepared according to the description of Example 1 of U.S. Patent No. 4,056,496 as follows:

On a water bath maintained at a temperature of 25° to 30°C., 1 kg. of isopropylidene glycerol methacrylate, 3 liters of distilled water, 6 g. of concentrated sulfuric acid and 0.4 g. of hydroquinone monomethyl ether were agitated for 16 hours. The reaction mixture was neutralized with barium hydroxide, and the resulting barium sulfate precipitate was separated by filtration. Sodium chloride was added to the filtrate till saturation, and the oil layer separated on the saturated salt water was extracted with an ether. To the extract was added anhydrous sodium sulfate and it was allowed to stand in a cold, dark place overnight. The extract was filtered, and the solvent was distilled under reduced pressure by an evaporator on a cold water bath to give colorless, transparent liquid glycerol methacrylate.

Water-absorptive contact lenses were prepared in the same manner as in Comparative Example 1 except that the glycerol methacrylate obtained in the above was employed. The lenses had a water content of 54.3%, an oxygen permeability of 1.72×10^{-10} ml.cm./cm.²sec.mmHg, a refractive index (n_D^{20}) of 1.404 and a visible ray percent transmission of more than 90%.

From the results obtained in Example 1 and Comparative Examples 1 and 2, it would be understood that the water-absorptive contact lens of the present invention has the highest water content.

EXAMPLE 2

There were mixed and dissolved 75 g. of IPGMA, 20 g. of 2-hydroxyethyl methacrylate (hereinafter referred to as "2-HEMA"), 5 g. of lauryl methacrylate (hereinafter referred to as "LMA") and 0.07 g. of ADMVN. The mixture was placed in a test tube. The thermal polymerization was carried out stepwise at 35°C. for 48 hours in a constant temperature water bath, and then at 50°C. for 8 hours, at 60°C. for 6 hours, at 80°C. for 6 hours, at 100°C. for 2 hours and finally at 110°C. for 2 hours in a hot air circulating dryer to give a polymer in the form of a rod. The rod was cut and polished in a usual manner to form into contact lenses.

The lenses were immersed in a 50% aqueous solution of formic acid for 30 minutes and then in 6N hydrochloric acid for 2 hours (or in 3.6N hydrochloric acid for 6 hours) to conduct the acid treatment. The lenses were then immersed in a 0.024% aqueous solution of sodium carbonate to conduct the neutralization treatment. The obtained water-absorptive contact lenses had a water content of 63.1%, an oxygen permeability of 2.27×10^{-10} ml.cm./cm.²sec.mmHg, a refractive index (n_D^{20}) of 1.390 and a visible ray percent transmission of more than 90%.

EXAMPLES 3 TO 5

Water-absorptive contact lenses were prepared in the same manner as in Example 2 except that respective components used in the copolymerization were employed in amounts shown in Table 1.

The results are shown in Table 1.

With respect to the IPGMA copolymer obtained in Example 3, infrared absorption spectrums of the copolymer before acid treatment and the copolymer after acid treatment were measured by employing infrared spectrophotometer Type A—202 made by Japan Spectroscopic Co., Ltd. The results are shown in the accompanying drawing in which numerals A and B are for the copolymer before acid treatment and for the copolymer after acid treatment. A clear increase of hydroxyl group is observed in the IPGMA copolymer treated with acid from the peak for hydroxyl group in the neighborhood of $3,400\text{ cm}^{-1}$, while the disappearance of the peak for the dioxolan ring in the neighborhood of 820 cm^{-1} is observed.

TABLE 1

	Example 3	Example 4	Example 5
<u>Components (g.)</u>			
IPGMA	75	60	40
2-HEMA	17.5	32	52
LMA	—	—	—
n-AMA* ¹	7	—	—
MMA	—	8	8
AMA* ²	0.5	—	0.3
Bis—S* ³	—	0.3	—
ADMVN	0.07	0.045	0.045
<u>Physical properties</u>			
Refractive index (n_D^{20})	1.395	1.403	1.421
Water content (%)	58.8	52.2	43.1
Oxygen permeability (ml.cm./cm. ² sec.mmHg)	2.00×10^{-10}	1.88×10^{-10}	1.38×10^{-10}
Visible ray percent transmission (%)	>90	>90	>90

(Note) *1 n-AMA: n-Amyl methacrylate

*2 AMA: Allyl methacrylate

*3 Bis-S: 4,4'-Dimethacryloyloxy-diphenyl sulfone

EXAMPLE 6

There were admixed and dissolved 67 g. of MEMA, 25 g. of 2-HEMA, 6 g. of LMA, 2 g. of MMA, 0.3 g. of ethylene glycol dimethacrylate (hereinafter referred to as "EDMA") and 0.07 g. of azobisisobutyronitrile (hereinafter referred to as "AIBN") as a polymerization initiator, and the mixture was placed in a test tube. The thermal polymerization was carried out stepwise first at 40°C. for 24 hours in a constant temperature water bath, and then at 50°C. for 8 hours, at 60°C. for 6 hrs, at 80°C. for 6 hours, at 100°C. for 3 hours and finally at 110°C. for 3 hours in a hot air circulating dryer to give polymer in the form of a rod. The rod was cut and polished in a usual manner to form into contact lenses, and subjected to the acid treatment and the neutralization treatment in the same manner as in Example 2 to give water-absorptive contact lenses. The lenses had a water content of 51.3%, an oxygen permeability of 1.64×10^{-10} ml.cm./cm.²sec.mmHg, a refractive index (n_D^{20}) of 1.407 and a visible ray percent transmission of more than 90%.

EXAMPLES 7 TO 9

Water-absorptive contact lenses were prepared in the same manner as in Example 6 except that the respective components used in the copolymerization were employed in amounts shown in Table 2. The results are shown in Table 2.

TABLE 2

Components (g.)	Example 7	Example 8	Example 9
MEMA	—	60	—
MBMA	67	—	60
2-HEMA	25	32	32
LMA	6	8	8
MMA	2	—	—
EDMA	0.3	—	—
AMA	—	0.3	0.3
AIBN	0.07	—	—
ADMVN	—	0.045	0.045
<u>Physical properties</u>			
Refractive index (n_D^{20})	1.409	1.411	1.411
Water content (%)	50.0	46.3	47.7
Oxygen permeability (ml.cm./cm. ² sec.mmHg)	1.73×10^{-10}	1.75×10^{-10}	1.59×10^{-10}
Visible ray percent transmission (%)	>90	>90	>90

EXAMPLE 10

There were admixed and dissolved 50 g. of MPMA, 44 g. of 2-HEMA, 6 g. of LMA, 0.3 g. of EDMA and 0.07 g. of ADMVN as a polymerization initiator, and the mixture was placed in a test tube. The thermal polymerization was carried out first at 35°C. for 48 hours in a constant temperature water bath and then carried out in a hot air circulating dryer at 45°C. for 16 hours, at 70°C. for 4 hours and at 90°C. for 4 hours, to give a polymer in the form of a rod. The rod was cut and polished in a usual manner to form into contact lenses. The lenses were subjected to the acid treatment and the neutralization treatment in the same manner as in Example 2 to give water-absorptive contact lenses. The thus obtained lenses had a water content of 35.8%, an oxygen permeability of 1.22×10^{-10} ml.cm./cm.²sec.mmHg, a refractive index (n_D^{20}) of 1.431 and a visible ray percent transmission of more than 90%.

EXAMPLES 11 AND 13

Water-absorptive contact lenses were prepared in the same manner as in Example 10 except that respective components in the polymerization were employed in amounts shown in Table 3. The results are shown in Table 3.

TABLE 3

	<u>Example 11</u>	<u>Example 12</u>	<u>Example 13</u>
<u>Components (g.)</u>			
MPMA	—	40	—
2-MSDD	50	—	40
2-HEMA	44	54	54
LMA	6	6	6
EDMA	0.3	—	—
Bis-S	—	0.3	0.3
ADMVN	0.07	0.07	0.07
<u>Physical properties</u>			
Refractive index (n_D^{20})	1.422	1.437	1.426
Water content (%)	42.4	34.8	39.5
Oxygen permeability (ml.cm./cm. ² sec.mmHg)	1.45×10^{-10}	1.16×10^{-10}	1.30×10^{-10}
Visible ray percent transmission (%)	>90	>90	>90

EXAMPLE 14

There were admixed and dissolved 70 g. of 3-MDIX, 25 g. of 2-HEMA, 4.5 g. of LMA, 0.5 g. of AMA and 0.07 g. of ADMVN as a polymerization initiator, and the mixture was placed in a test tube. The thermal polymerization was carried out stepwise first at 40°C. for 24 hours in a constant temperature water bath, and then at 50°C. for 8 hours, at 60°C. for 6 hours, at 80°C. for 6 hours, at 100°C. for 3 hours and at 110°C. for 3 hours in a hot air circulating dryer to give polymer in the form of a rod. The rod was cut and polished in a usual manner to form into contact lenses, and they were subjected to the acid treatment and the neutralization treatment in the same manner as in Example 2 to give water-absorptive contact lenses. The lenses had a water content of 72.0%, an oxygen permeability of 2.76×10^{-10} ml.cm./cm.²sec.mmHg, a refractive index (n_D^{20}) of 1.374 and a visible ray percent transmission of more than 90%.

EXAMPLES 15 TO 17

Water-absorptive contact lenses were prepared in the same manner as in Example 14 except that the respective components used in the copolymerization were employed in amounts shown in Table 4. The results are shown in Table 4.

TABLE 4

	Example 15	Example 16	Example 17
<u>Components (g.)</u>			
3-MDIX	67	50	60
2-HEMA	25	44	32
LMA	6	6	8
MMA	2	—	—
EDMA	0.3	0.3	—
AMA	—	—	0.3
ADMVN	0.07	0.07	0.07
<u>Physical properties</u>			
Refractive index (n_D^{20})	1.384	1.394	1.387
Water content (%)	64.5	58.6	63.5
Oxygen permeability (ml.cm./cm. ² sec.mmHg)	2.55×10^{-10}	2.30×10^{-10}	2.44×10^{-10}
Visible ray percent transmission (%)	>90	>90	>90

EXAMPLE 18

In a monomer mixture of 70 g. of IPGMA, 6 g. of LMA, 2 g. of MMA and 0.2 g. of AMA were dissolved 5 g. of polypropylene glycol having an average molecular weight of 3,000 as a wetting agent and 0.03 g. of ADMVN as a polymerization initiator. The mixture was placed in a molding container consisting of male and female molds corresponding to the shape of a contact lens, and the polymerization was carried out stepwise at 35°C. for 48 hours, at 50°C. for 4 hours and at 60°C. for 8 hours in a hot air circulating dryer. After removing the molds, the molding in the shape of a contact lens was immersed in a 50% aqueous solution of formic acid for 30 minutes and in 6N hydrochloric acid for 2 hours. The acid-treated lens was then immersed in a 0.024% aqueous solution of sodium carbonate to neutralize the acid in the lens, and was further immersed and boiled in a 0.9% physiological saline water for 3 hours. This boiling treatment was conducted twice. The thus obtained water-absorptive contact lens had a water content of 89.6%, an oxygen permeability of 4.50×10^{-10} ml.cm./cm.²sec.mmHg, a refractive index (n_D^{20}) of 1.350 and a visible ray percent transmission of more than 90%.

EXAMPLE 19

A water-absorptive contact lens was prepared in the same manner as in Example 14 by employing 70 g. of IPGMA, 6 g. of ALIPG, 15 g. of 2-HEMA, 6 g. of LMA, 2 g. of MMA, 0.2 g. of AMA and 0.07 g. of ADMVN. The obtained lens had a water content of 60.2%, an oxygen permeability of 2.46×10^{-10} ml.cm./cm.²sec.mmHg, a refractive index (n_D^{20}) of 1.391 and a visible ray percent transmission of more than 90%.

EXAMPLE 20

The polymerization was carried out under the same condition as in Example 14 by employing 33.5 g. of IPGMA, 33.5 g. of MEMA, 25 g. of 2-HEMA, 6 g. of LMA, 2 g. of MMA, 0.3 g. of EDMA and 0.2 g. of ADMVN, to give a transparent polymer in the form of a rod. The rod was cut and polished in a usual manner to form into a contact lens. The lens was immersed in 4N hydrochloric acid for 4 hours, and the thus acid-treated lens was then immersed in a 0.024% aqueous solution of sodium carbonate to neutralize the acid in the lens. The obtained water-absorptive contact lens had a water content of 50.0%, an oxygen permeability

of 1.63×10^{-10} ml.cm./cm.²sec.mmHg, a refractive index (n_D^{20}) of 1.408 and a visible ray percent transmission of more than 90%.

EXAMPLE 21

5 A water-absorptive contact lens was prepared in the same manner as in Example 20 except that 25 g. of MEMA, 25 g. of 3-MDIX, 44 g. of 2-HEMA, 6 g. of LMA, 0.3 g. of EDMA and 0.2 g. of ADMVN were employed and the acid treatment was carried out in 2N hydrochloric acid for 3 hours. 5

The lens had a water content of 52.5%, an oxygen permeability of 1.69×10^{-10} ml.cm./cm.²sec.mmHg, a refractive index (n_D^{20}) of 1.403 and a visible ray percent transmission of more than 90%.

10 EXAMPLE 22

The polymerization was carried out under the same condition as in Example 14 by employing 100 g. of a mixture (hereinafter referred to as "UK") of DMDO and IPGMA in a weight ratio of 82:18, 0.5 g. of AMA, 0.2 g. of EDMA and 0.1 g. of ADMVN, to give a transparent polymer in the form of a rod. The rod was cut and polished in a usual manner to form into a contact lens. The lens was immersed in a 15 50% aqueous solution of formic acid for 20 minutes and then in 6N hydrochloric acid for 1 hour. The acid-treated lens was then immersed in a 0.024% aqueous solution of sodium carbonate to neutralize the acid. 15

The thus obtained water-absorptive contact lens had a water content of 75.7%, an oxygen permeability of 2.75×10^{-10} ml.cm./cm.²sec.mmHg, a refractive index (n_D^{20}) of 1.370 and a visible ray percent transmission of more than 90%. 20

EXAMPLES 23 AND 24

Water-absorptive contact lenses were prepared in the same manner as in Example 22 except that the respective components in the polymerization were employed in amounts shown in Table 5.

The results are shown in Table 5.

TABLE 5

	Example 23	Example 24
<u>Components (g.)</u>		
UK	92	47.5
(DMDO)	(75.7)	(39.1)
(IPGMA)	(16.3)	(8.4)
2-HEMA	—	47.5
LMA	3	5
MMA	5	—
AMA	0.5	0.5
EDMA	0.2	0.2
ADMVN	0.1	0.1
<u>Physical properties</u>		
Refractive index (n_D^{20})	1.392	1.427
Water content (%)	61.2	42.2
Oxygen permeability (ml.cm./cm. ² sec.mmHg)	2.19×10^{-10}	1.42×10^{-10}
Visible ray percent transmission (%)	>90	>90

EXAMPLE 25

The polymerization was carried out under the same condition as in Example 14 by employing 85 g. of IPGMA, 15 g. of MMA, 0.5 g. of EDMA and 0.2 g. of ADMVN, to give a polymer in the form of a rod. The rod was cut and polished in a usual manner to form into a contact lens. The lens was immersed in a 40% aqueous solution of formic acid for 20 minutes and in 3N hydrochloric acid for 40 minutes. The acid-treated lens was then immersed in a 0.024% aqueous solution of sodium carbonate to neutralize the acid in the lens and was then boiled for 1 hour in a 0.9% physiological saline water to give a water-absorptive contact lens.

The lens had a water content of 55.8%, an oxygen permeability of 2.00×10^{-10} ml.cm./cm.²sec.mmHg, a refractive index (n_D^{20}) of 1.399 and a visible ray percent transmission of more than 90%.

EXAMPLE 26

A water-absorptive contact lens was prepared in the same manner as in Example 25 by employing 80 g. of IPGMA, 5 g. of 2-HEMA, 15 g. of MMA, 0.5 g. of EDMA and 0.2 g. of ADMVN.

The contact lens had a water content of 53.4%, an oxygen permeability of 1.70×10^{-10} ml.cm./cm.²sec.mmHg, a refractive index (n_D^{20}) of 1.401 and a visible ray percent transmission of more than 90%.

EXAMPLE 27

The polymerization was carried out under the same condition as in Example 14 by employing 15 g. of IPGMA, 15 g. of ALIPG, 15 g. of 1,2:5,6-di-O-isopropylidene-3-O-methacryloyl-D-glucofuranoside (hereinafter referred to as "MDG"), 40 g. of 2-HEMA, 15 g. of MMA, 0.2 g. of AMA and 0.2 g. of ADMVN, to give a polymer in the form of a rod. The rod was cut and polished in a usual manner to form into a contact lens. The lens was immersed in 2N hydrochloric acid for 3 hours, and the acid-treated lens was subjected to the neutralization treatment by immersing in a 0.024% aqueous solution of sodium carbonate to give the desired water-absorptive contact lens.

The lens had a water content of 64.1%, an oxygen permeability of 2.35×10^{-10} ml.cm./cm.²sec.mmHg, a refractive index (n_D^{20}) of 1.385 and a visible ray percent transmission of more than 90%.

EXAMPLES 28 TO 31

Water-absorptive contact lenses were prepared in the same manner as in Example 27 except that the respective components used in the polymerization were employed in amounts shown in Table 6.

The results are shown in Table 6.

TABLE 6

	Example 28	Example 29	Example 30	Example 31
Components (g.)				
IPGMA	15	15	—	—
3-MDIX	—	—	15	—
MEMA	—	—	—	15
ALIPG	—	15	15	15
MDG	15	—	15	15
6-MDIGA*	—	15	—	—
2-HEMA	55	40	40	40
MMA	15	15	15	15
AMA	0.2	0.2	0.2	0.2
ADMVN	0.2	0.2	0.2	0.2

TABLE 6 (continued)

	Example 28	Example 29	Example 30	Example 31
<u>Components (g.)</u>				
<u>Physical properties</u>				
Refractive index (n_D^{20})	1.402	1.397	1.402	1.402
Water content (%)	52.8	58.6	53.2	53.0
Oxygen permeability (ml.cm./cm. ² sec.mmHg)	1.70×10^{-10}	2.22×10^{-10}	1.80×10^{-10}	1.73×10^{-10}
Visible ray percent transmission (%)	>90	>90	>90	>90

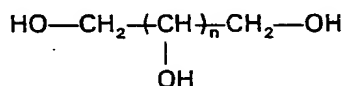
(Note) *6-MDIGA: 1,2:3,4-di-O-isopropylidene-6-O-methacryloyl-D-galactopyranoside

The contact lenses obtained in Example 16 were continuously worn on the right eyes of 3 albino rabbits for 21 days. No change was observed on the corneal surfaces and also no decrease of glycogen was observed. Further, in respect of the histological observation, there was no vascularization, substantial edema and infiltration of inflammatory cells, and no morphologically significant change was observed between the right eye and the comparative left eye.

In addition to the components used in the Examples, other components can be used in the Examples as set forth in the specification to obtain substantially the same results.

CLAIMS

- 10 1. A water-absorptive contact lens prepared by a process which comprises the steps of carrying out a polymerization of a monomer mixture containing a monomer having a ketalized glycitol and at least one member selected from the group consisting of a hydrophilic monomer and a hydrophobic monomer, forming the resulting copolymer into a contact lens, treating the contact lens with an acid and replacing the acid impregnated in the resulting water-absorptive contact lens with water or a physiological saline water. 10
- 15 2. The contact lens of Claim 1, wherein said monomer having a ketalized glycitol is a member selected from the group consisting of an ester compound of a ketalized glycitol with an ethylenically unsaturated carboxylic acid and an ether compound of a ketalized glycitol with an ethylenically unsaturated alcohol. 15
- 20 3. The contact lens of Claim 2, wherein said ketalized glycitol is a ketal derived from a glycitol having the general formula: 20

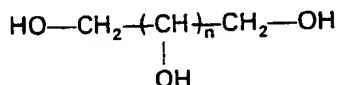


wherein n is an integer of 1 to 5.

- 25 4. The contact lens of Claim 1, wherein said hydrophilic monomer is at least one member selected from the group consisting of 2-hydroxyethyl methacrylate, 2-hydroxyethyl acrylate, 2-hydroxypropyl methacrylate, 2-hydroxypropyl acrylate, polyethylene glycol monomethacrylate, polyethylene glycol monoacrylate, methacrylamide, acrylamide, dimethylmethacrylamide, dimethylacrylamide, methacrylic acid, acrylic acid and N-vinyl pyrrolidone. 25
- 30 5. The contact lens of Claim 1, wherein said hydrophobic monomer is at least one member selected from the group consisting of alkyl esters of methacrylic acid and acrylic acid wherein the alkyl group has 1 to 15 carbon atoms, vinyl esters of methacrylic and acrylic acids, allyl esters of methacrylic and acrylic acids, alkyl esters of itaconic and crotonic acids, vinyl esters of aliphatic carboxylic acids, styrene and acrylonitrile. 30
- 35 6. A process for preparing a water-absorptive contact lens which comprises the steps of carrying out a polymerization of a monomer mixture containing a monomer having a ketalized glycitol and at least one member selected from the group consisting of a hydrophilic monomer and a hydrophobic monomer, forming the obtained copolymer into a contact lens, treating the contact lens with an acid, and replacing the acid impregnated in the resulting water-absorptive contact lens with water or a physiological saline water. 35

7. The process of Claim 6, wherein said monomer having a ketalized glycitol is a member selected from the group consisting of an ester compound of a ketalized glycitol with an ethylenically unsaturated carboxylic acid and an ether compound of a ketalized glycitol with an ethylenically unsaturated alcohol.

5 8. The process of Claim 7, wherein said ketalized glycitol is a ketal derived from a glycitol having the general formula: 5



wherein n is an integer of 1 to 5.

10 9. The process of Claim 6, wherein said hydrophilic monomer is at least one member selected from the group consisting of 2-hydroxyethyl methacrylate, 2-hydroxyethyl acrylate, 2-hydroxypropyl methacrylate, 2-hydroxypropyl acrylate, polyethylene glycol monomethacrylate, polyethylene glycol monoacrylate, methacrylamide, acrylamide, dimethylmethacrylamide, dimethylacrylamide, methacrylic acid, acrylic acid and N-vinyl pyrrolidone. 10

15 10. The process of Claim 6, wherein said hydrophobic monomer is at least one member selected from the group consisting of alkyl esters of methacrylic acid and acrylic acid wherein the alkyl group has 1 to 15 carbon atoms, vinyl esters of methacrylic and acrylic acids, allyl esters of methacrylic and acrylic acids, alkyl esters of itaconic and crotonic acids, vinyl esters of aliphatic carboxylic acids, styrene and acrylonitrile. 15

11. The process of Claim 6, wherein the polymerization is carried out in the presence of a wetting agent.

20 12. A water-absorptive contact lens prepared by a process which comprises the steps of carrying out a polymerization of a monomer mixture containing a monomer having a ketalized glycitol and at least one member selected from the group consisting of a hydrophilic monomer and a hydrophobic monomer, substantially as described with reference to the accompanying drawings. 20

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